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Electroplating of Al on Mg alloy in a dimethyl sulfone-aluminum chloride bath

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Abstract

Electroplating of Al on a Mg alloy using a dimethyl sulfone-aluminum chloride bath was studied. Although dense and uniform Al films were electrodeposited on the Mg alloy from the bath at 110°C, the adhesion of the Al film was poor when the electrodeposition was carried out directly onto the bare alloy. Subjecting the Mg alloy to zincate pretreatment resulted in Al films with good adhesion. The adhesion strength of the Al films was measured using a pull-off test. The fractured interface was observed with SEM-EDX, which revealed that the Mg alloy substrate reacted with the bath before the electrodeposition of Al started. The reaction products formed on the substrate were detrimental to the adhesion of the electrodeposited Al film. The improved corrosion resistance of the Al-coated Mg alloy was confirmed by measuring polarization curves in a 3.5 wt. % NaCl solution.

Keywords: Electrodeposition, Non-aqueous bath, Zincate treatment, Adhesion, Corrosion resistance

1. Introduction

Mg alloys containing Al and Zn (AZ series) are attracting increasing attention in various industries, such as automobile, aerospace, and mobile electronics, owing to their desirable properties, namely, low density and a high strength-to-weight ratio [1]. However, these alloys have poor corrosion resistance, which limits their application [2]. Several surface treatments to enhance the corrosion resistance of Mg alloys have been studied, including anodization, chemical conversion coating, organic coating, and metal coating [3]. Among these, electroplating of Al has the advantage of being a low energy-consuming process that yields a smooth metallic protective coating. Because various surface treatments of Al, such as anodization and electrolysis coloration, are already well established, further surface functionalization by these techniques should be feasible after the electroplating of Al. Furthermore, Al coating maintains the recyclability of the Mg alloys, because Al is a primary alloying element for the widely used AZ series of Mg alloys [4].

Since the electrodeposition of Al is not feasible in aqueous solutions, the use of certain non-aqueous media, such as molten salts [5, 6], organic solvents [7, 8], and ionic liquids [4, 9-16] is required. The electrodeposition of Al and Al alloys on Mg alloy substrates has been studied using ionic liquids [4, 17-24] and molten salts [25, 26]. However, a dimethyl sulfone ($DMSO_2$)-aluminum chloride ($AlCl_3$) system, which is an organic solvent bath, has certain advantages over the above-mentioned media: It is much cheaper than ionic liquids, and yet more stable and less volatile (boiling point 238 °C) than other organic solvents, such as ethers and aromatic hydrocarbons. In addition, it can be used at a lower temperature (110 °C) than the molten salts (>140 °C). It has been demonstrated that dense, uniform Al coatings with high corrosion resistance can be electrodeposited in a $DMSO_2$-$AlCl_3$ bath [27-35]. The electrodeposition can be performed at higher rates (40-80 mA cm^{-2}) in this bath than in ionic liquids without dendritic growth. However, the electrodeposition of Al on the Mg alloy in a $DMSO_2$-$AlCl_3$ bath has not previously been explored.

In this study, we investigate the feasibility of electroplating Al onto a Mg alloy in a $DMSO_2$-$AlCl_3$ bath. It has been reported that in the case of Al electrodeposition from molten salts and ionic liquids, a zincate pretreatment [21, 24, 25, 36] of Mg alloys or electrodeposition at a low temperature [19] is required to ensure an adequate adhesion of the Al coating onto the Mg alloy substrates. However, quantitative information about the adhesion strength of the coatings is limited. In this study, adhesion strength was measured using a pull-off test (ASTM D4541), and a procedure for formation of Al coatings with good adhesion on the Mg alloy was demonstrated.

2. Experimental section

A Mg alloy plate (AZ61; Gonda Metal) composed of 6.52 wt. % Al, 1.06 wt. % Zn, 0.256 wt. % Mn, and the balance Mg was used as the substrate for electrodeposition. The substrate (35 mm × 35 mm × 1 mm) was polished with SiC paper (P#600), washed with water and ethanol, and subsequently air-dried. A part of the substrate was covered with PTFE tape, so that only a certain area (12 mm × 12 mm) would be exposed.

Zincate treatment of the Mg alloy substrate was conducted as follows [37]: the substrate was immersed in an aqueous solution containing 0.19 M HCl and 0.125 M NaF for 30 s to remove the surface oxide layer, and then transferred without drying into an aqueous solution containing 0.16 M $ZnSO_4$, 0.103 M NaF, 0.047 M Na_2CO_3, and 0.421 M $K_4P_2O_7$, where it was kept for 1 h to form a zinc layer on the surface.

The electrodeposition of Al was carried out in an argon-filled glove box equipped with a circulation system. The electrolytic bath was prepared by mixing $DMSO_2$ (99%, Tokyo Chemical Industry, Japan) and anhydrous $AlCl_3$ grains (Fluka, crystallized, 99%) at a molar ratio of 10:2. A glass vessel with a volume of 150 mL was used as an electrolytic cell. The aforementioned Mg alloy substrate and an Al plate were used as the cathode and anode, respectively. They were placed in the cell so that the interelectrode gap was 100 mm. The electrodeposition of Al was performed galvanostatically at 60 mA cm^{-2} and 110°C for 800 s with an electrochemical analyzer (ALS, model 660 C). The electrolyte was stirred by a magnetic stirrer at 100 rpm during the electrodeposition. After the electrodeposition, the substrate with Al deposit was washed with distilled water.

A scanning electron microscope (SEM; S-3500, Hitachi) combined with energy-dispersive X-ray spectroscopy (EDX; INCAxact, Oxford Instruments) was used to observe the morphology and measure the elemental composition of the coatings on the substrate. X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (X'pertPRO-MPD, PANalytical) with Cu $K\alpha$ radiation. The adhesion of the electrodeposited Al films onto the substrate was estimated by the tape test (JIS H 8504) and the pull-off test (ASTM D4541) using an adhesion tester (PosiTest AT-A Automatic, Defelsco). In the pull-off test, an aluminum dolly (10 mmφ) was attached to the surface of the Al film with an acrylic adhesive (AY-123, Cemedine). After the adhesive was fully cured, the Al film was cut around the dolly, and then a pull-off load was applied to the dolly. The load at which the dolly was separated from the substrate was measured (adhesion strength). To evaluate the corrosion resistance of the bare and the Al-coated Mg alloys, potentiodynamic polarization curves were measured in 3.5 wt. % NaCl aqueous solution deaerated by N_2 bubbling. A platinum wire and a Ag/AgCl electrode in 3.3 M

KCl solution were used as the counter and the reference electrodes, respectively. The potential was scanned from –1.5 V to –0.5 V at a sweep rate of 0.5 mV s^{-1}.

3. Results and discussion

Galvanostatic electrodeposition performed directly on a bare Mg alloy substrate in the $DMSO_2$-$AlCl_3$ bath yielded a white Al film on the substrate. The Al film, however, had blisters and did not adhere to the substrate; it was completely peeled off in the tape test. As will be discussed later in detail, this weak adhesion is due to a spontaneous reaction of the Mg alloy substrate with the bath components. This reaction occurs immediately after the substrate is immersed in the bath, and before the electrodeposition is performed. The reaction product formed on the substrate is detrimental to the adhesion of the Al film. Similar phenomena have been observed in cases that use molten salts [25].

In order to protect the Mg alloy substrate from reacting with the bath, zincate treatment [37, 38] was conducted on the substrate prior to the Al electrodeposition. Comparison of the SEM images of the substrate surface before and after the zincate treatment (Figs. 1a and b), along with EDX analysis, showed that the substrate surface was uniformly covered with fine Zn grains following the zincate treatment. The electrodeposition on the zincated substrate, under the same conditions as above, yielded an Al film without blisters. Figure 1c presents a surface SEM image of the Al film on the zincated substrate, showing that the Al film is composed of randomly oriented crystal grains, approximately 3 μm in size. The cross-sectional image (Fig. 1d) confirms that a dense Al layer (~17 μm in thickness) and a thin Zn layer are stacked firmly on the Mg alloy substrate.

As shown in Figure 2, the XRD patterns of the substrate before and after the zincate treatment and after the electrodeposition of Al confirm that the grains generated by the zincate treatment on the substrate were Zn metal and the film formed by the electrodeposition was composed of Al metal. Unlike the Al film electrodeposited on the bare substrate, the film formed on the zincated substrate had no blisters and was not peeled off by the tape test. Notably, the films electrodeposited on the substrate that were pre-treated in the zincate solution for less than 1 h did not have adequate adhesion to pass the tape test. The zincate treatment for at least 1 h was required to obtain an Al film with adequate adhesion to pass the tape test.

The pull-off test was performed to quantify the adhesion strength of the Al films electrodeposited onto the zincated Mg alloy substrate. The Al film shown above as a typical example was delaminated from the substrate at a tensile stress of 2.5 MPa. Figure 3 presents SEM images of the fractured surfaces caused by the test, revealing the interface

where the adhesion failure occurred. Table I summarizes the compositions at the locations identified in the SEM images. The SEM images, along with the composition analysis, show that the fractured surface of the film was basically composed of Al (spot 1 in Fig. 3a), while that of the substrate was primarily covered with Zn (spot 3 in Fig. 3b). This indicates that the delamination occurred mainly at the interface between the Al film and Zn layer on the substrate. The SEM image of the substrate surface after the pull-off test revealed some dark areas (spot 4 in Fig. 3b), which were not observed before the electrodeposition (Fig. 1b). Compared with the composition of the major part of the substrate surface (spot 3 in Fig. 3b), the Zn content in the dark areas (spot 4 in Fig. 3b) was low, while the O content was high. In addition, C, S, and Cl were detected in the dark areas, although those were not detected in the other areas. On the backside of the peeled Al film, grains with similar compositional features, i.e., high C, O, and Cl contents, were also found (spot 2 in Fig. 3a), indicating that the dark substance was brittle and fractured during the pull-off test. C, O, S, and Cl originate from the components of the $DMSO_2$-$AlCl_3$ bath. The presence of these elements suggests the formation of an organic compound from the reaction between the bath and the substrate. Legrand et al. reported that Al metal stored in a $DMSO_2$-$AlCl_3$ bath gradually corroded as a result of the reduction of $DMSO_2$, and Al, O, S and Cl were detected in the corrosion product [39]. Because Mg is more reactive than Al, the Mg alloy substrate could corrode quickly in the bath. It is suggested that the organic compound found on the substrate is the product of corrosion, which occurs where the Mg alloy substrate is not fully covered with the Zn layer. The corrosion of the substrate occurs immediately after the substrate is immersed into the bath, and continues until the substrate surface is covered by the electrodeposited Al layer.

To better understand the effect of corrosion on adhesion, we examined Al films electrodeposited onto zincated Mg alloy after it was immersed in the plating bath for various time periods (t_h), without potential being applied. The adhesion strengths of the resulting Al films are summarized in Table II, which indicates that the adhesion increases with decreasing t_h. The Al films electrodeposited with $t_h \geq 10$ s delaminated at the interface between the Al film and the Zn layer. In contrast, the Al film prepared with t_h = 3 s did not delaminate, but a bond failure occurred between the Al film and the adhesive used to fix the film to the dolly at a tensile stress of 5.3 MPa, indicating an adhesion strength greater than 5.3 MPa.

Figure 4 shows the SEM images of the fractured interfaces of the substrate after the pull-off test, confirming that the amount of the corrosion product (appearing dark) formed on the substrate increases with increasing t_h. These results show that the poor

adhesion of the Al films electrodeposited on the Mg alloy substrate is due to the corrosion product generated on the substrate before the electrodeposition. The zincate treatment improved the adhesion because the Zn layer formed on the substrate hindered the corrosion. The Zn layer has pits and cannot prevent corrosion completely. Therefore, it is necessary for the Al electrodeposition to begin quickly after the immersion of the substrate into the bath to ensure adequate adhesion. It should be noted that, contrary to expectation, the Al film electrodeposited with t_h = 0 s had weaker adhesion and was peeled off at a stress of 0.5 MPa. This weak adhesion was probably due to a decrease in the bath temperature at the vicinity of the substrate, which is caused by immersing the substrate at room temperature into the bath at 110°C. Electrodeposition at low temperatures is prone to generate a coarse, burnt Al deposit with poor adhesion.

The effect of the Al coating on corrosion resistance was examined by comparing the polarization curves for the Al-coated Mg alloy and bare Mg alloy in 3.5 wt. % NaCl solution (Fig. 5). Curve (a) in Figure 5 shows that the bare Mg alloy undergoes active dissolution when a potential of –1.3 V is applied. On the other hand, Curve (b) shows passivation behavior up to a potential of –0.66 V with current densities of $<10^{-5}$ A cm^{-2} followed by a passivation breakdown. The passivation is caused by the formation of an oxide protective layer on the surface of the Al film, and the passivation breakdown is most likely due to pitting corrosion in the presence of Cl^- ions. The wide passivation range with the low current density is a typical behavior of pure Al, indicating that there was no significant pinhole in the Al film. The passivation current density and the pitting potential observed in this study are almost in agreement with the values reported for the Al films electrodeposited on Mg alloys from the EMIC-$AlCl_3$ ionic liquid [4, 17, 24] and on Al-Mn alloys from molten salts [25]. This result demonstrates that the Al film electrodeposited from the $DMSO_2$-$AlCl_3$ bath can effectively prevent the Mg alloy substrate from rapid corrosion.

4. Conclusions

The Al films electrodeposited directly onto the bare Mg alloy substrate in the $DMSO_2$-$AlCl_3$ bath had poor adhesion. However, Al films with good adhesion were obtained by performing zincate pretreatment on the Mg alloy substrate. The pull-off adhesion tests revealed that the adhesion strength of the Al films increased with the decrease of the period during which the substrate was immersed in the $DMSO_2$-$AlCl_3$ bath, without applying potential, before the electrodeposition started. This fact, along with SEM-EDX observations on the fractured interface resulting from the pull-off test, indicate that the Mg alloy substrate reacts with the bath at the pits of the Zn layer before

Al electrodeposition is initiated. The reaction products formed on the substrate are detrimental to the adhesion of the Al film. This study confirmed that the corrosion resistance of the Mg alloy is improved by the electrodeposition of Al from the $DMSO_2$-$AlCl_3$ bath.

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Figure captions

Fig. 1: SEM images of the surfaces of the Mg alloy substrate (a) before and (b) after zincate treatment, and (c) surface and (d) cross-section of the zincated substrate after Al film electrodeposition.

Fig. 2: XRD patterns of (a) bare Mg alloy substrate, (b) zincated substrate, and (c) electrodeposited Al film on the zincated substrate.

Fig. 3: SEM images of the fractured surfaces of (a) electrodeposited film and (b) substrate resulting from the pull-off test.

Fig. 4: SEM images of the fractured interface of the Mg alloy substrate resulting from the pull-off test, after electrodeposition of Al films. The Al films were electrodeposited after the substrate was immersed in the plating bath, without potential being applied, for (a) 20 s, (b) 30 s, and (c) 60 s.

Fig. 5: Polarization curves for (a) bare Mg alloy and (b) Mg alloy covered with electrodeposited Al in 3.5 wt. % NaCl solution.

Table I

Composition analysis of the fractured interface resulting from the pull-off test.

Interface	Position[a]	Content (at.%)[b]						
		Mg	Al	Zn	C	O	S	Cl
Film side	1	0.0	96.0	0.0	0.0	4.0	0.0	0.0
Film side	2	7.0	10.5	16.2	24.0	40.4	0.0	1.9
Substrate side	3	47.5	4.8	38.6	0.0	9.1	0.0	0.0
Substrate side	4	19.7	0.4	1.3	15.8	60.8	0.7	1.3

[a] The analyzed positions are indicated in Fig. 3.

[b] The reliability of the O content determined by EDX is low.

Table II

Adhesion strength of Al films electrodeposited onto zincated Mg alloy after it was immersed for various periods in the plating bath, without potential being applied.

Immersion time (t_h)	Adhesion strength (MPa)
3	>5.3
20	2.5
30	2.1
60	1.2

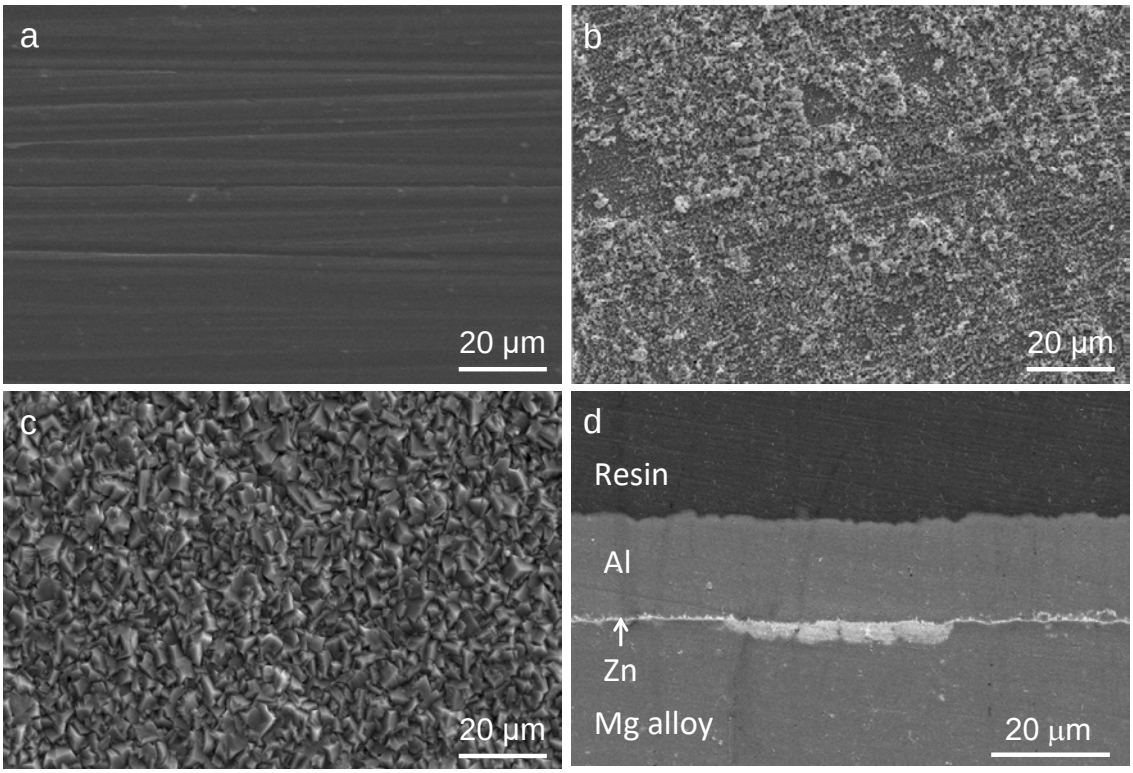

Fig. 1

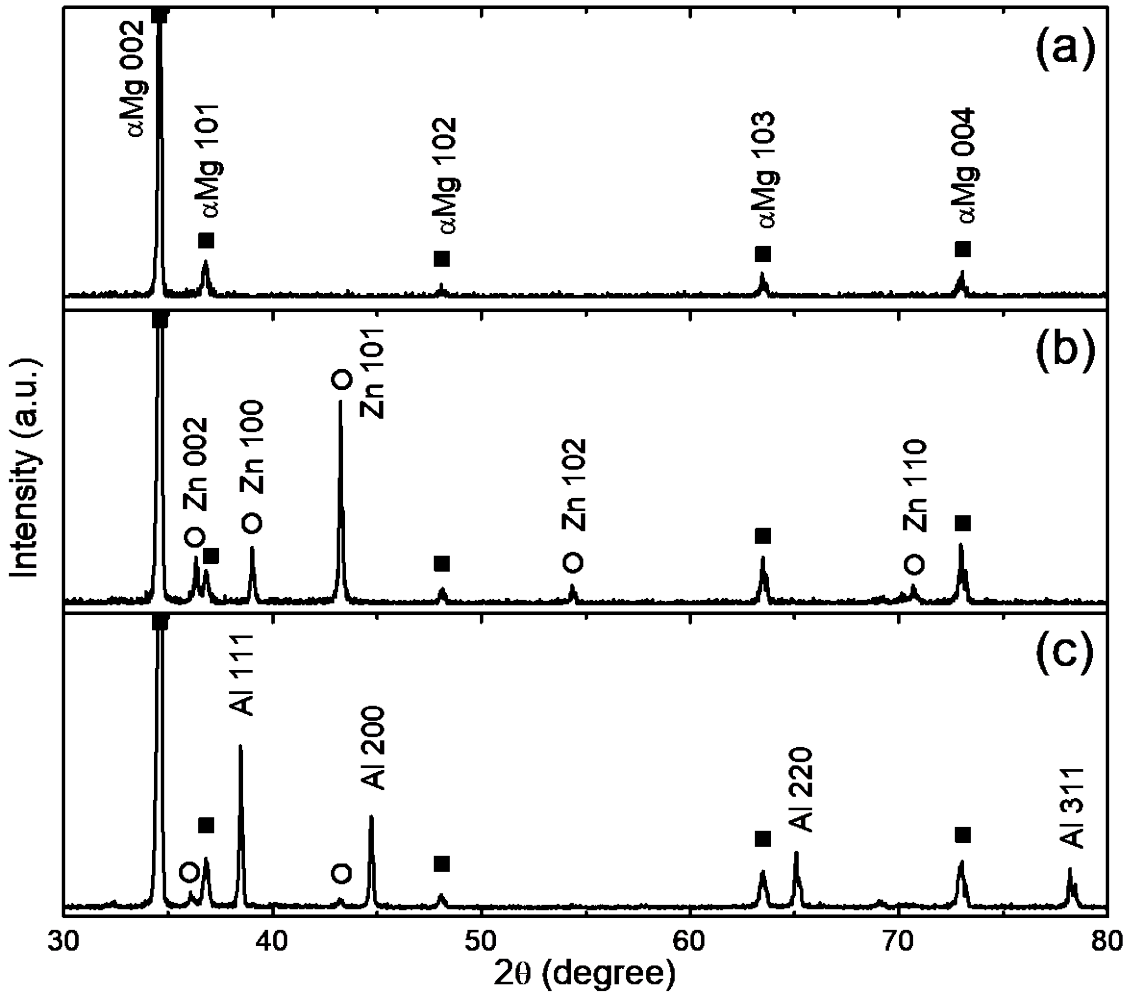

Fig. 2

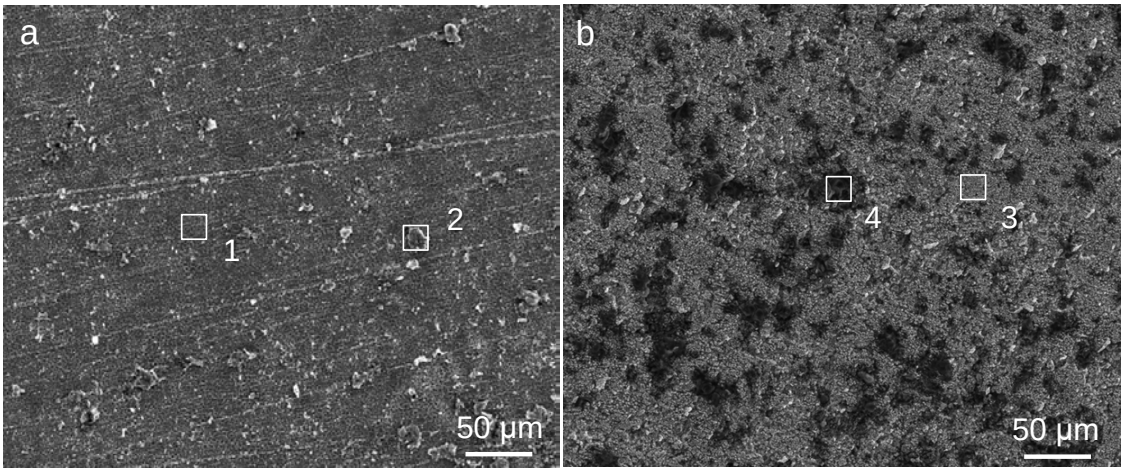

Fig. 3

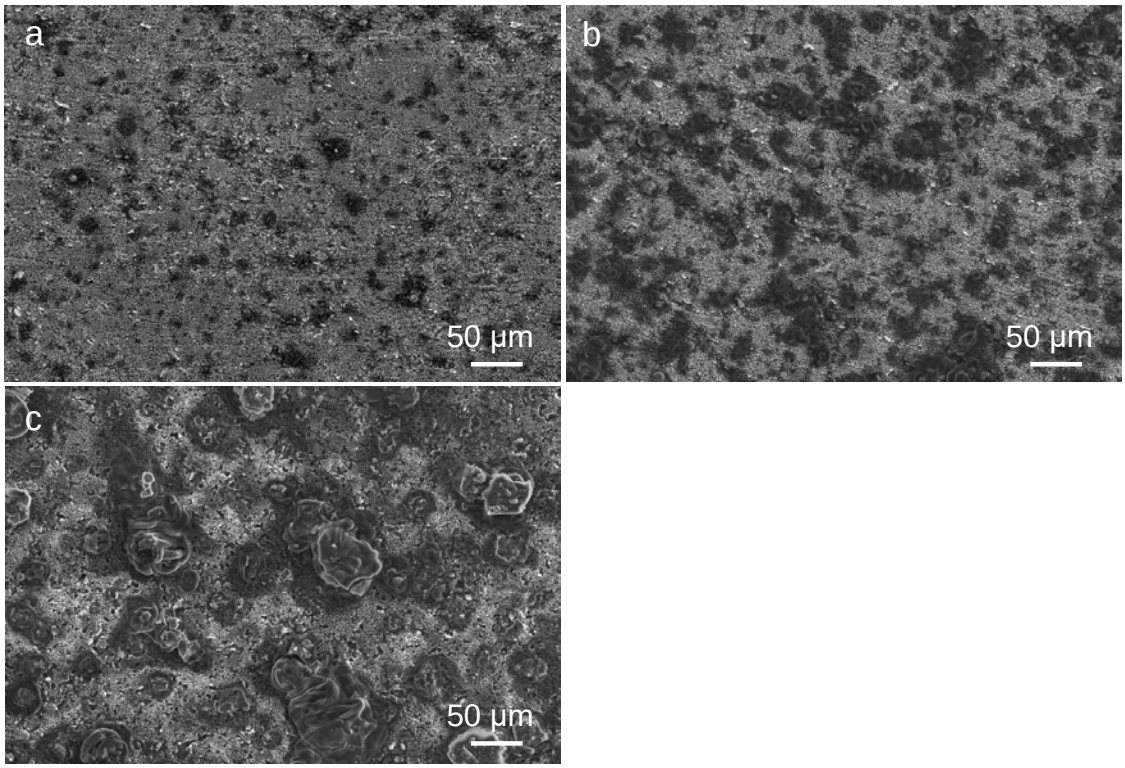

Fig. 4

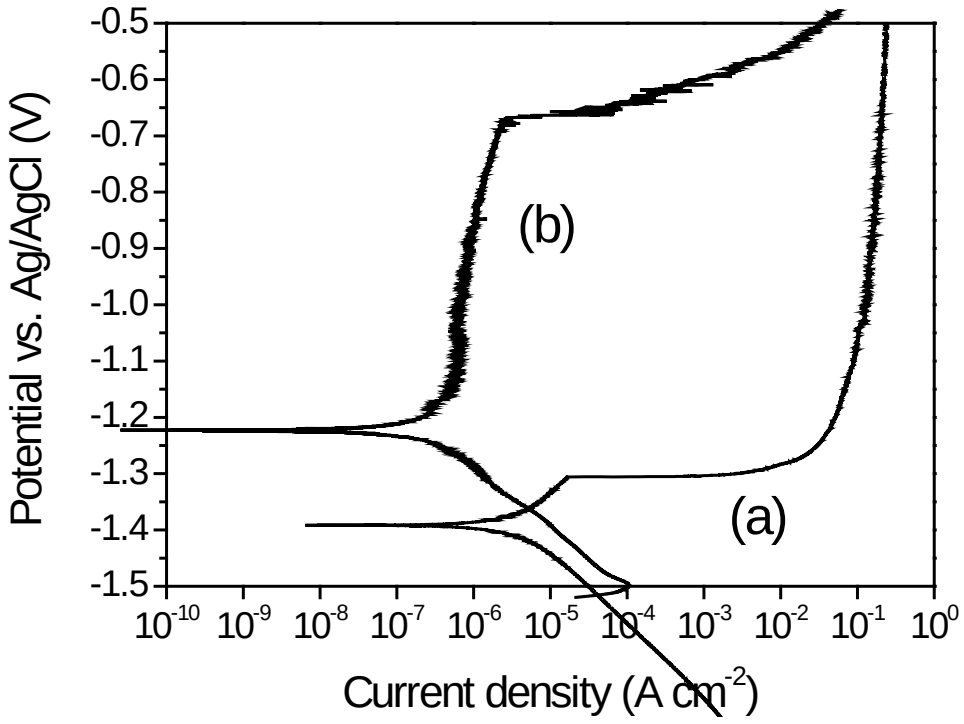

Fig. 5